Electronic Copy Only

Title: ACID DIGESTION OF SOLIDS [Method EPA 3050B]

Approvals (Signature/Date):

[redacted]

Facility Distribution No. ___________ **Distributed To:**________________________

1.0 Scope and Application

1.1 This is a strong acid digestion procedure for the preparation of sediments, sludge, soils, and other types of solid materials by EPA Method 3050B for analysis by inductively coupled plasma atomic emission spectroscopy (ICP) or inductively coupled plasma-mass spectrometry (ICP/MS).

1.2 Method 3050B is designed to determine the concentration of “environmentally available” metals, and is not a true “total metals” digestion (see discussion below). The procedure is used primarily for hazardous waste characterization and other Resource Conservation and Recovery Act (RCRA) compliance testing.

1.3 The elements approved for Method 3050B are shown in Table I. The source method also mentions that other elements may be prepared by the method if the quality control requirements are met. The complete list of elements routinely included in this procedure by TestAmerica Denver is shown in Table II.

1.4 If sample preparation utilizing the Incremental Sampling Method is required, see SOP DV-OP-0013 for the procedure required prior to acid digestion for metals incorporating this procedure.

2.0 Summary of Method

A representative 1 to 2 gram portion of sample is digested with two cycles of nitric acid additions, followed by hydrogen peroxide digestion. For ICP analysis, the sample is also refluxed with hydrochloric acid. The resulting solution is filtered and diluted to 100 mL with reagent water. For the Incremental Sampling Method, 10 g of sample is used and brought to a final volume of 500 ml.

3.0 Definitions

3.1 Refer to the Glossary of the TestAmerica Denver Quality Assurance Manual (QAM) and policy DV-QA-003P, Quality Control Program, for definitions of general analytical and QA/QC terms.

3.2 **Total Metals -** Although Method 3050B is often referred to as a “total metals” digestion, it is important to understand that there are many compounds formed from these elements that are not efficiently dissolved using this digestion procedure. It is more accurately termed a strong acid digestion procedure. The limitations are discussed further in Section 4 (Interferences) below. The method itself states, “This method is not a total digestion technique for most samples.” There are a variety of total digestion procedures used for metal assay, geochemical analysis, etc., that involve more vigorous digestions than 3050B.

3.3 **Preparation Batch -** A group of up to 20 samples that are of the same matrix and are processed together using the same lots of reagents and standards. The minimum QC elements in a batch are outlined in Section 9.

3.4 **Reagent Water –** Water that is free of the analytes of interest. In the Metals group, reagent water is obtained from a Barnstead E-Pure water purification system.

3.5 Other quality control terminology used in this procedure is based on SW-846, and is defined in the glossary section of the TestAmerica Denver Quality Assurance Manual (QAM) and Policy DV-QA-003P, *Quality Control Program*.

4.0 Interferences

4.1 There are common compounds formed by the elements of interest (e.g., barium sulfate, beryllium oxide, silicon dioxide, crystalline silicates, titanium dioxide, etc.) that are not efficiently dissolved using this EPA approved procedure.

4.2 Silicon or silica are occasionally requested as part of the Method 3050B digestion. However, this digestion will include only acid-soluble silicon, and will not dissolve crystalline silica. The analysis is for silicon, but the final result is sometimes expressed as silica rather than silicon.

4.3 Antimony and silver have poor solubility in dilute nitric acid solution. Therefore it is strongly recommended that these elements are determined by the ICP-MS procedure that includes HCl as the final digestion acid. See Section 11.12 of this SOP.

4.4 Potential sources of trace metals contamination include metallic or metal-containing labware (e.g., powdered gloves which contain high levels of zinc), containers, impure reagents, dirty glassware, improper sample transfers, dirty work areas, atmospheric inputs such as dirt and dust, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them. See Attachment 1 for more information regarding contaminant control.

4.5 The entire work area, including the bench top and fume hood, should be thoroughly cleaned on a routine schedule in order to minimize the potential for environmental contamination.

4.6 For critical low-level determinations of boron and silica, only quartz and/or plastic labware should be used.

4.7 Physical interference effects may contribute to inaccuracies in the determinations of trace elements. Oils, solvents, and other matrix materials may not be digested using these methods if they are not soluble in acids. If physical interferences are present, they should be documented.

4.8 Allowing samples to boil or go dry during digestion may result in the loss of volatile metals or conversion of metals to insoluble forms. For example, antimony is easily lost by volatilization from hydrochloric media. If this occurs the sample must be re-prepared.

4.9 Visual interferences or anomalies (such as foaming, emulsions, precipitates, etc.) must be documented.

4.10 Samples Requiring Additional Digestion Reagents

A few examples of types of samples that might require additional digestion reagents follow. It is very important to note situations where samples are not

behaving normally. However, do not assume that adding additional reagents will be acceptable for the project, even if it is obvious that the digestion will be incomplete without it. The situation must be discussed with the project manager and documented in a Nonconformance Memo (NCM), whether or not the variations suggested in the following examples are approved.

4.10.1 Samples with high organic content may require additional nitric acid and/or hydrogen peroxide for a thorough digestion, but these oxidizing reagents should be added very carefully to avoid violent reactions.

4.10.2 Samples with high concentrations of metal in the elemental form or refractory oxides may require additional hydrochloric acid for a thorough digestion. As an example, blasting sand used to remove paint from the hull of ships typically consists of 30% cupric oxide. Following 3050B exactly will produce results as low as 0.1% without additional hydrochloric acid. Increasing the volume of hydrochloric acid can produce results approaching the true copper concentration. Samples that appear to have nonstandard matrices or have visible metal particles should be documented in an NCM.

4.10.3 Highly alkaline materials may require larger volumes of acid than specified in this procedure.

4.10.4 If the use of extra digestion reagents is approved, the same volume of reagents must be added to all field samples and QC samples in the batch. Usually the method blank results will not be elevated. To ensure that the QC sample results accurately reflect sample results, the QC samples must be treated exactly like the samples.

5.0 Safety

5.1 Employees must abide by the policies and procedures in the Environmental Health and Safety Manual, Radiation Safety Manual and this document.

5.2 This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, nitrile or latex gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.3 Specific Safety Concerns or Requirements

5.3.1 Samples that contain high concentrations of carbonates or organic materials or samples that are at elevated pH can react violently when acids are added. If any solid sample appears to be a chemical substance rather than an environmental sample, consult with the group supervisor or the Project Manager (PM) before adding acid.

5.3.2 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile gloves must be worn while handling samples, standards, solvents, and

reagents. Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

5.4 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit(2)	Signs and Symptoms of Exposure
Hydrogen Peroxide, H_2O_2	Oxidizer Corrosive Poison	1 ppm TWA 1.4 mg/m^3 TWA 75 ppm IDLH	Contact with other materials may cause fire. Eye contact may result in permanent eye damage. Causes eye and skin burns. Corrosive: May cause severe respiratory tract irritation. Harmful if swallowed, may cause digestive tract irritation or burns.
Nitric Acid, HNO_3	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid, HCl	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
(1) Always add acid to water to prevent violent reactions. (2) Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

All equipment IDs for any support equipment (pipettes, thermometers, etc.) must be recorded in the batch record.

6.1 Instrumentation

6.1.1 Top-loading balance capable of accurately weighing to the nearest 0.01 grams.

Note: Balances are serviced annually and the accuracy checked daily using three standard masses. See SOP DV-QA-0014 for details.

6.1.2 Digestion "Hot Block" or equivalent heating device capable of maintaining a temperature of 90-95 °C. The Hot Block temperature must be monitored separately for each unit. The temperature of each Hot Block is checked by placing a calibrated thermometer through a cap on a digestion tube that is partially filled with water. The water in the tube must be high enough to cover the thermometer past the minimum immersion line. The temperature is directly recorded in the Batch Information area in the TestAmerica LIMS (TALS).

6.2 Supplies

6.2.1 Thermometers (non-mercury liquid filled or digital) that cover a temperature range including 80-110 °C with clearly visible 1 °C increments.

Note: Thermometers are calibrated before use and periodically as described in SOP DV-QA-0001.

6.2.2 Disposable digestion tubes, with volume accuracy verified to ± 3% gravimetrically prior to use. See SOP DV-QA-0008.

6.2.3 Watch glasses, ribbed or equivalent, or disposable digestion tube covers.

6.2.4 Whatman 541 (acid washed) filter paper, or equivalent.

6.2.5 Whatman GD/XP - PVDF membrane, 0.45-micron syringe filters, No. 6973-2504, for trace metal analysis, or equivalent. When used to filter any sample in a preparation batch or analytical batch, filters of the same type are also used to filter the method blank and the LCS in the batch. Acceptable results for the QC samples demonstrate that the filters neither add nor subtract analytes.

6.2.6 Syringes or equivalent filtration apparatus.

6.2.7 Disposable plastic funnels.

6.2.8 Disposable wooden spatulas for subsampling.

6.2.9 Centrifuge, capable of at least 2,000 rpm.

6.2.10 Graduated cylinders, 100 mL and 500 mL, capable of $\pm$ 3% accuracy.

6.2.11 Calibrated automatic pipettes with corresponding pipette tips or Class A glass volumetric pipettes.

Note: Mechanical pipettes are calibrated before use as described in SOP DV-QA-0008.

6.2.12 Class A volumetric flasks.

6.2.13 pH indicator strips (pH range 0 – 6).

6.3 Computer Software and Hardware

Please refer to the master list of documents, software and hardware located on R:\QA\Read\Master List of Documents\Master List of Documents, Software and Hardware.xls or current revision for the current software and hardware to be used for data processing.

7.0 Reagents and Standards

Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.1 Reagent water – Millipore DI system or equivalent, 10-18.2 megohm-cm. See SOP DV-QA-0026 for daily water monitoring procedure.

7.2 Nitric acid (HNO_3), concentrated - Trace metal grade or better.

7.3 Nitric acid (HNO_3), 5% - Add 50 mL of concentrated HNO_3 to approximately 900 mL of reagent water and dilute to 1 liter.

7.4 Hydrochloric acid (HCl), concentrated - Trace metal grade or better.

7.5 30% Hydrogen peroxide (H_2O_2) - Reagent grade used for ICP analysis.

7.6 30% Hydrogen peroxide (H_2O_2) – Ultra pure used for ICP-MS analysis.

7.7 Glass beads, $\leq$ 1 mm diameter, washed with aqua regia (for DoD projects).

7.8 Standards

7.8.1 All standards must be NIST traceable. Unless purchased directly from NIST, the accuracy of each standard is verified before the initial use, as described in SOP DV-QA-0015.

7.8.2 Storage and Shelf Life of Metal Standards

7.8.2.1 Standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. They are stored at room temperature.

7.8.2.2 Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.8.3 LCS and MS Spike Solutions

7.8.3.1 ICP and ICP/MS spike solutions are purchased as custom-made solutions from a commercial vendor at ready-to-use concentrations. No further dilutions are needed.

7.8.3.2 If a non-routine element is required that is not contained in the custom-made solution, single-element solutions from a commercial vendor may also be used.

7.8.3.3 Intermediate standards prepared in the laboratory may be used for spiking as long as the procedures for standard recording and verification outlined in SOP DV-QA-0015 are followed.

Typical LCS and MS/MSD spike standard concentrations are shown below.Analysis	Standard	Elements	Conc. (mg/L)
ICP	ICP SPK 3A	Ag, Be, Cd Cr Cu Co, Mn, Ni, Pb, V, Zn As, Fe, Li, Sr, Th Al, Ba, Bi, Se, Tl, U P Ca, K, Mg, Na	5 10 20 25 50 100 200 1,000 5,000
ICP	ICP SPK 2B	Sb, Zr B, Mo, Ti Sn, S Si (SiO_2)	50 100 200 1,000 (2,140)

Typical LCS and MS/MSD spike standard concentrations are shown below.Analysis	Standard	Elements	Conc. (mg/L)
ICP-MS	MS CALSTD-1	Ag, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, Th, Tl, U, V, Zn	20
ICP-MS	MS spike 2	Mo, Sb, Sn, W, Zr Al, Fe	20 200

Note: ICP or ICP-MS digestions may select different combinations of spikes in order to satisfy client requests. All spikes used for sample digestion will be recorded in the Reagent module in TALS.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Sample holding time for metals included under the scope of this SOP is 180 days from the date of collection to the date of analysis.

8.2 Soil samples do not require chemical preservation, but are stored at ≤6 °C until the time of analysis.

Matrix	Sample Container	Min. Sample Size	Preservation[1]	Holding Time[2]	Reference
Soils	Glass	3 grams	Cool ≤ 6 °C	180 Days	N/A

[1] Although ICP analysis of soil does not require refrigeration of the samples, mercury analysis does require refrigeration. Samples which will be used to aliquot for both analyses must be refrigerated.

[2] Inclusive of digestion and analysis.

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the LIMS Method Comments to determine specific QC requirements that apply. For SOPs that address only preparation, QC acceptance limits on the analytical results are not included. Refer to the appropriate SOP that describes the determinative method.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver policy DV-QA-003P, *Quality Control Program*.

9.1.2 Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), etc., are described in TestAmerica Denver policy DV-QA-024P, *QA/QC Requirements for Federal Programs*. This procedure meets all criteria for DoD QSM 5.0

unless otherwise stated. Any deviation or exceptions from QSM 5.0 requirements must have prior approval in the project requirements.

9.1.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via Method Comments in the LIMS and the Quality Assurance Summaries (QAS) in the public folders.

9.1.4 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.2 Preparation batches may consist of up to 20 field samples. Laboratory generated QC samples (method blanks, LCS, MS/MSD) are not counted towards the maximum 20 samples in a batch. Field QC samples are included in the batch count.

9.3 Minimum QC Requirements

Each preparation batch must contain a method blank (MB), a laboratory control sample (LCS), and a matrix spike/matrix spike duplicate (MS/MSD) pair. Note that some programs require an unspiked duplicate sample in place of or in addition to the duplicate matrix spike. Be sure to check special instructions in TALS. If clients specify specific samples for the MS and MSD, the batch may contain multiple MS/MSD pairs.

9.3.1 Method Blank (MB)

One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. Soil method blanks are prepared by taking 5 mL or 5 g of reagent water through the procedure described in Section 11. Add 1.0 g of prewashed glass beads to the blank if required by the client to better simulate a solid matrix.

The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data.

Acceptance Criteria: Criteria for the acceptance of blanks are contained within the individual analytical method SOPs.

Corrective Action: If the method blank does not meet the criteria contained within the analytical method SOPs, the blank and all associated samples in the batch must be re-digested and reanalyzed.

9.3.2 Laboratory Control Sample (LCS)

One aqueous LCS must be processed with each preparation batch. The LCS contains reagent water that is spiked with all the analytes of interest and is carried through the entire analytical procedure. A duplicate LCS (LCSD) must be prepared when there is insufficient sample volume to perform an MS/MSD. The LCS is used to monitor the accuracy of the analytical process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. Add 1.0 g of prewashed glass beads to the LCS if required by the client to better simulate a solid matrix.

The spike solutions described in Section 7.8.3 are used to prepare LCSs as follows:

- Routine ICP: Add 1.0 mL of spike
- DoD ICP: Add 1.0 mL of spike to 1.0 g of glass beads
- Routine ICP-MS: Add 1.0 mL of spike
- DoD ICP-MS: Add 1.0 mL of spike to 1.0 g of glass beads

The resulting spike concentrations for each element are given in Table 2 and Table 3.

Incremental Sampling Method LCSs are spiked with 5 ml of spike.

Acceptance Criteria: Criteria for the acceptance of LCS results are contained within the individual analytical method SOPs.

Corrective Action: When LCS results fail to meet control limits, the LCS and all associated samples in the batch must be re-prepared and reanalyzed.

9.3.3 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a second aliquot of a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a third aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Samples identified as field blanks cannot be used for MS/MSD analysis. The MS/MSD results are used to determine the effect of a

matrix on the precision and accuracy of the analytical process.

The spike solution described in Section 7.7.3 is also used to prepare matrix spikes, as follows:

- ICP: Add 1.0 mL of spike
- ICP-MS: Add 1.0 mL of spike

The resulting spike concentrations for each element are given in Tables II through IV. Incremental Sampling Method MS/MSD pairs are spiked with 5 ml of spike.

NOTE 1: The spike must be added after the sample aliquot but before any reagents.

NOTE 2: This method does not require a sample duplicate. Precision is measured using the MS/MSD. Use of the MS/MSD precision is preferred as not all samples will contain measurable concentrations of the target analytes. Samples that have target analytes at low concentrations or non-detectable levels do not provide useful precision data. When an MS/MSD pair is not available, an LCS and LCSD are used to measure precision.

10.0 Calibration

Not applicable. This SOP addresses sample preparation only for subsequent ICP or ICP/MS analysis. Calibration of the measurement system is covered in the SOPs for the determinative methods.

11.0 Procedure

11.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

11.2 Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

11.3 Sample Custody

11.3.1 Samples are transferred from the Sample Control group to the Metals group and the transfer is documented using the Sample Transfer function of the Internal Chain of Custody in TALS (see SOP DV-QA-0003 for details).

11.3.2 Proper sample identification is extremely important in any preparation procedure. Labeling of digestion tubes and bottles must be done in a manner to ensure connection with the proper sample.

11.4 Subsampling

11.4.1 It is not acceptable to simply collect 1.0 g off of the top of the sample. Samples must be mixed and incrementally subsampled to obtain a representative portion. At a minimum, mix by stirring with a disposable wooden spatula. If there is insufficient room in the sample container to allow for proper mixing, refer to SOP DV-QA-0023, *Subsampling*, for directions.

11.4.2 Select at least three incremental subsamples from different locations in the original sample and place them in a tared 50 mL digestion tube. The final sample weight should be between 1.0 and 1.5 g. Record the weight to the nearest 0.01 g.

11.4.3 Measure additional aliquots for QC samples required in the batch and spike as required (see Section 9 for details).

NOTE: When adding glass beads to the Method Blank and LCS digestion tubes, the nominal weight must be entered into the Initial Amount field in TALS. The true weight of glass beads should be recorded in the Notes field on the Worksheet tab in the preparation batch.

11.5 Incremental Sampling Method Digestion

For the Incremental Sampling Method approximately 10 g of sample is weighed out by the Organic Prep group following the procedure described in SOP DV-OP-0013. This pre-weighed sample is then delivered to the Metals group for digestion and analysis. The sample weight is recorded on the ISM Worksheet and attached to the incremental sampling batch in TALS. The pre-weighed aliquots are delivered in 125 mL digestion tubes which are ready for spike standards and reagents to be added. The Method 3050B digestion reagents are increased 5x to maintain the same proportions as are used for a 1-2 gram sample. When required, 10 g of glass beads are added to the Method Blank and LCS prior to digestion.

11.6 Initial Digestion Cycle with 1:1 Nitric Acid

11.6.1 Add approximately 5 mL of reagent water to each digestion tube.

11.6.2 Add 5 mL of concentrated HNO_3.

11.6.3 After all of the acid has been added to the preparation batch, gently swirl the samples to mix and then place the sample rack on the Hot Block.

11.6.4 Place a ribbed cover on each tube.

11.6.5 Heat samples to 90-95 °C, and reflux for 15 minutes without boiling.

NOTE: **DO NOT ALLOW SAMPLES TO BOIL OR GO DRY** during any part of the digestion. Doing so will result in the loss of analyte and the sample must be re-prepared.

11.6.6 Remove the samples from the Hot Block and allow them to cool before proceeding with the next step.

11.6.7 Record the start time, starting temperature, end time, and ending temperature in TALS.

11.7 Second Digestion Cycle Using Concentrated Nitric Acid

11.7.1 Add 5 mL of concentrated HNO_3, and replace the ribbed cover.

11.7.2 Place samples back on the Hot Block and reflux at 90-95 °C for 30 minutes. Add reagent water as needed to ensure that the volume of solution is not reduced to less than 5 mL.

11.7.3 If brown fumes are observed, this means that material in the sample is actively being oxidized. There may not be enough HNO_3 acid to complete the oxidation, and there could be violent reaction of the sample with peroxide in the third digestion step. For that reason, it is necessary to repeat the previous two steps until no more fumes are evolved.

11.7.4 Heat the samples at 90-95 °C for 2 hours.

11.7.5 Allow the samples to thoroughly cool before proceeding.

11.8 Third Digestion Cycle Using Hydrogen Peroxide

11.8.1 Add 2 mL of reagent water to each tube.

11.8.2 Add 3 mL of 30% H_2O_2 a few drops at a time. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence.

11.8.3 Replace the ribbed cover and heat samples until effervescence subsides.

11.8.4 Allow the samples to cool.

11.8.5 Continue adding 30% H_2O_2 in 1 mL increments with warming until

effervescence is minimal or sample appearance is unchanged. If additional peroxide is added to a sample then it must also be added to the method blank and LCS.

NOTE: Do not add more than a total of 10 mL of 30% H_2O_2. If 10 mL have been added and the samples are still vigorously effervescing, document the situation with an NCM and continue with the digestion.

11.8.6 Heat the samples at 90-95 °C for 2 hours.

11.8.7 Allow the samples to cool.

11.8.8 If samples will be analyzed by ICP, continue on with the fourth digestion step using HCl in Section 11.8. If the samples will be analyzed by ICP-MS, skip the HCl digestion step and go to step 11.10.

11.9 Fourth Digestion Cycle for ICP Using Concentrated Hydrochloric Acid

11.9.1 If the samples are being prepared for ICP analysis, add 10 mL of concentrated HCl to the samples in the digestion tubes and cover with ribbed covers.

11.9.2 Reflux for an additional 15 minutes without boiling.

11.9.3 Allow the samples to cool.

11.10 Separating Undigested Solids from the Digestion Solution

11.10.1 Filter samples through Whatman 541 or equivalent fiber filters into a graduated 125 mL digestion tube whose accuracy is documented to be better than ± 3%.

NOTE: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.10.2 For samples digested by the Incremental Sampling Method use a 500 mL poly bottle that has been measured after measuring out 500 mL of DI water from a graduated cylinder.

11.10.3 Wash the original digestion tube and ribbed cover with reagent water to ensure quantitative transfer of all of the digestion solution into the new digestion tube.

11.10.4 Rinse the funnel and filter paper with reagent water to ensure complete sample transfer into the new digestion tube.

11.10.5 Re-volume sample to 100 mL with reagent water. This must be done volumetrically, rather than by weight. Record the final volume in TALS. For Multi-Incremental samples the final volume is 500 mL.

11.11 Documentation and Record Management

The following information must be recorded for each preparation batch. This information is directly entered into TALS.

- Initial sample weight and final digestion volume
- Preparation analyst and date
- Identification of all reagents and standards
- Identification of all measuring and test equipment used (e.g., balances, thermometers, pipettes)
- Glass beads lot number
- Filter paper lot number
- Digestion tube lot number
- Hot Block ID number
- Fume Hood ID number

11.12 Alternate Antimony Preparation for Analysis by ICP-MS

11.12.1 Weigh out 1.0-1.5 g soil samples according to the procedure in Section 11.3.

11.12.2 Add approximately 5 mL of reagent water to each digestion tube.

11.12.3 Spike the LCS, LCSD, MS, and MSD with 1.0 mL of the MS spike 2 standard.

11.12.4 Add 2.5 mL concentrated HNO_3 and 2.5 mL concentrated HCl to each sample and batch QC.

11.12.5 Cover each tube with a watch glass and reflux on hot block at 90-95 °C for 15 minutes.

11.12.6 Filter through Whatman 541 or equivalent filter paper into a new 125 mL digestion tube while still hot.

11.12.7 Rinse the filter and funnel with 1.25 ml of hot (~95 °C) concentrated HCl.

11.12.8 Rinse three times with hot (~95 °C) reagent water (5 mL rinses.)

11.12.9 Place the filter paper and soil residue back into the original sample digestion vessel. Add 2.5 mL concentrated HCl, cover and reflux on the hot block for 20 minutes or until paper dissolves.

11.12.10 Filter through a fresh filter into the original filtrate. Rinse three times with reagent water (5 mL rinses).

11.12.11 Bring to final volume of 100 mL with reagent water.

12.0 Calculations / Data Reduction

Not applicable. Calculations of final results are described in the determinative analytical SOPs.

13.0 Method Performance

13.1 Method Detection Limit (MDL)

An MDL must be determined for each analyte/matrix prior to the analysis of any samples. See the SOPs for the determinative analysis methods for details.

13.2 Demonstration of Capabilities

All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows.

13.2.1 Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid-level calibration.

13.2.2 Calculate the average recovery and standard deviation of the recovery for each analyte of interest.

13.2.3 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. TNI 2009 requires consecutive passing results. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.2.4 Until the IDOC is approved by the QA Manager (or designee); the trainer and trainee must be identified in the batch record.

13.2.5 Further details concerning demonstrations of proficiency are described in SOP DV-QA-0024.

13.3 Training Requirements

The group leader or supervisor is responsible for ensuring that this procedure is performed by an associate who has been properly trained in its use and has the required experience. A new analyst must be working under supervision prior to approval of the IDOC. Documentation that a new analyst is performing under supervision must be entered in the batch record (View Batch Information)until that analyst's IDOC has been approved by the QA Manager (or designee). See

requirements for demonstration of analyst proficiency in SOP DV-QA-0024.

14.0 Pollution Control

14.1 It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, order chemicals based on quantity needed, and prepare reagents based on anticipated usage and reagent stability).

14.2 Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards and reagents requiring disposal.

15.0 Waste Management

15.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in Section 13, *Waste Management and Pollution Prevention*, of the Environmental Health and Safety Manual, and DV-HS-001P, *Waste Management Program*.

15.2 The following waste streams are produced when this method is carried out:

15.2.1 Aqueous Acidic (Metals) - Corrosive – Waste Stream J

15.2.2 Radioactive waste, mixed waste, and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Radioactive Waste Coordinator for proper management of these materials.

16.0 References

16.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, December 1996; Method 3050B.

16.2 Department of Defense Quality Systems Manual for Environmental Laboratories, Final Version 4.2, 10/25/2010.

16.3 Department of Defense Quality Systems Manual for Environmental Laboratories Version 5.0, July 2013.

17.0 Method Modifications:

Item	Method	Modification
1	3050B	Method 3050B Section 7.1 states that a 1-2 g aliquot is to be used. The amount specified by TestAmerica Denver in this procedure is limited to 1-1.5 g in order to prevent increased instrument maintenance and sample reruns due to dilutions.

18.0 Figures, Tables, and Attachments

Table 1: Method 3050B Approved Analyte List for ICP/ICP-MS

Table 2: Soil LCS and MS/MSD Spikes for ICP

Table 3: Soil LCS and MS/MSD Spikes for ICP-MS

Attachment 1: Contamination Control Guidelines

19.0 Revision History

- Revision 10 dated 31 October 2017
    - Annual Review
- Revision 9 dated 31 October 2016
    - Annual Review
    - Update the temperature heating range to 90-95°C where stated in the SOP
    - Removed the reference to AFCEE throughout SOP
    - Added current section 3.1 – reference to QAM for general definitions
    - Restructured and renumbered section 6.0
    - Added initial paragraph to section 6.0 regarding the documentation of equipment IDs
    - Revised the current sections 6.1 and 6.2 to reflect consistent verbiage and formatting as other SOPs
    - Added current section 7.6 Ultra Pure Peroxide reference
    - Added current footnote 1 to the section 8 table regarding soil preservation
    - Re-numbered previous footnote 1 to be footnote 2 to the section 8 table
    - Updated section 9.1 and subsections to reflect current practices and verbiage
    - Re-numbered Notes in section 9.3.3 to be Note 1 and Note 2
    - Added LCSD required when an MS/MSD is not available to sections 9.3.2 and 9.3.3 Note 2
    - Renumbered and updated section 11.1 and 11.2 to reflect current practices and verbiage
    - Added current section 11.2
    - Updated section 13.2 to reflect current practices and verbiage
    - Added Strontium to Table 3
    - Removed Titanium and Zirconium from Table 3
- Revision 8 dated 31 October 2015
    - Annual Review
    - Edited Sections 9.5.1 and 9.5.2 to clarify glass bead requirement
    - Added definition of reagent water
    - Updated Section 11.6.4 and 11.7.6 to reflect current practice
    - Removed Method exception 1 regarding method blank limits as it no longer applies
    - Added detail to training requirements for new analysts Section 13.3
    - Added note to Section 9.5.3 regarding precision requirements
    - Added note to Section 11.3 regarding recording of glass bead weights

- Revision 7 dated 31 March 2015
    - Annual Review
    - In Section 11.7.8 the section referenced was updated to 11.8
    - Updated spike standard name to MS spike 2 in Section 11.11.3
    - Formatting and grammar corrections throughout
    - Section 6.4 removed reference to calibrating digestion tubes
    - Section 6.6 changed name of filter paper to match current practice
    - Section 6.14 added to define computer systems used
    - Sections 7.7.3.1 and 7.7.3.2 combined
    - New Sections 7.7.3.2 - 7.7.3.4 added to define spikes used
    - Table of spike names and concentrations added to Section 7.7.3.4
    - Changed LIMS to TALS throughout
    - Section 8.2 changed storage temperature to ≤6 °C
    - Deleted Section 9.3, duplicated in 13.2
    - Added new Section 9.3 to address federal requirements
    - Rewrote Section 9.5
    - Changed Sections 9.6 – 9.8 to be subsections of the new 9.5
    - Rewrote Section 11.2.1
    - Removed method modification 2 because it referred to the analytical SOP
    - Created new method modification 2 explaining the 1-1.5 g sample aliquot
    - Section 11.3.2 changed required sample aliquot to 1-1.5 g to help avoid targeting
    - Rewrote Section 11.4 to define and explain the Incremental Sampling Method
    - Added new Section 11.5.3 to explain sample mixing
    - Section 11.7.5 added language to note regarding samples that require more than 10 mL of H2O2
    - Added detail into Sections 11.9.1 – 11.9.5
    - Folded Section 11.10.1 into 11.10
    - Rewrote list of data to be entered into TALS in Section 11.10
    - Rewrote Section 13.2 to match boilerplate
    - Deleted flowcharts Figures 1 and 2
    - Corrected element list in Table 2

- Revision 6 dated 31 March 2014
    - Annual Review
    - Formatting changes throughout document
    - Added to Section 11.7.5 to add additional peroxide to QC if added to samples
    - Updated section number in text to 11.8 in section 11.7.8
    - Added references for DoD QSM
    - Removed Attachment 2

- Revision 5 dated 04 March 2013
    - Section 7.7.3.1 Added DoD to the glass beads requirement
    - Section 11.11.2 Added that 5ml of water is added to the samples
    - Section 11.11.3 Changed spike name to 200.8 Cal-2
    - Updated spike level to 1.0ml in Table 3
    - Updated work instructions to current revision.
    - Formatting changes throughout document

- Revision 4 dated 3 February 2012

- Changed references of Multi-Incremental Sampling to Incremental Sampling Method throughout document
- Section 2.0 Added reference to Incremental Sampling Method
- Section 6.4 Added 50 mL digestion tubes
- Added introductory statement to section 7.0 regarding reagent purity
- Section 7.1 Updated acceptable criteria for the reagent water
- Section 9.7.2 Added LCS Incremental Sampling Method spike amounts
- Section 9.8.2 Added MS/MSD Incremental Sampling Method spike amounts
- Section 11.4 Updated sample amount for Incremental Sampling Method to 1 10g aliquot
- Section 11.9 Added Incremental Sampling Method final volume

- Revision 3.5, dated 24 August 2011
    - A note has been added to section 9.8.3 for the addition of the LCS/MS spike before reagents.

Earlier revision histories have been archived and are available upon request.

Table 1.

Method 3050B Approved Analyte List for ICP/ICP-MS

Element	Symbol	CAS Number
Aluminum	Al	7429-90-5
Antimony	Sb	7440-36-0
Arsenic	As	7440-38-2
Barium	Ba	7440-39-3
Beryllium	Be	7440-41-7
Cadmium	Cd	7440-43-9
Calcium	Ca	7440-70-2
Chromium	Cr	7440-47-3
Cobalt	Co	7440-48-4
Copper	Cu	7440-50-8
Iron	Fe	7439-89-6
Lead	Pb	7439-92-1
Magnesium	Mg	7439-95-4
Manganese	Mn	7439-96-5
Molybdenum	Mo	7439-98-7
Nickel	Ni	7440-02-0
Potassium	K	7440-09-7
Selenium	Se	7782-49-2
Silver	Ag	7440-22-4
Sodium	Na	7440-23-5
Thallium	Tl	7440-28-0
Vanadium	V	7440-62-2
Zinc	Zn	7440-66-6

Table 2.

Soil LCS and MS/MSD Spikes for ICP

ELEMENT	Stock Standard (mg/L)	Sample Spike (mg/kg)	Final Digested Solution (mg/L)
Aluminum	200	200	2.0
Antimony	50	50	0.5
Arsenic	100	100	1.0
Barium	200	200	2.0
Beryllium	5	5	0.050
Bismuth	200	200	2
Boron	100	100	1.0
Cadmium	10	10	0.1
Calcium	5,000	5,000	50.
Chromium	20	20	0.20
Cobalt	50	50	0.50
Copper	25	25	0.25
Iron	100	100	1.0
Lead	50	50	0.50
Lithium	100	100	1.0
Magnesium	5,000	5,000	50.
Manganese	50	50	0.50
Molybdenum	100	100	1.0
Nickel	50	50	0.50
Phosphorous	1,000	1,000	10.
Potassium	5,000	5,000	50.
Selenium	200	200	2.0
Silicon	1,000	1,000	10.
Silver	5	5	0.050
Sodium	5,000	5,000	50
Strontium	100	100	1.0
Sulfur	200	200	2.0
Thallium	200	200	2.0
Thorium	100	100	1.0
Tin	200	200	2.0
Titanium	100	100	1.0
Uranium	200	200	2.0
Vanadium	50	50	0.50
Zinc	50	50	0.50
Zirconium	50	50	0.5

NOTE: Final soil spike concentration based on the addition of 1.0 mL stock standard to 1.0 g of sample, which is then digested to produce a 100 mL final volume.

Table 3.

Soil LCS and MS/MSD Spikes for ICP-MS

ELEMENT	Stock Standard (mg/L)	Sample Spike (mg/kg)	Final Digested Solution (µg/L)
Aluminum	200	200	2,000
Antimony	20	20	200
Arsenic	20	20	200
Barium	20	20	200
Beryllium	20	20	200
Cadmium	20	20	200
Chromium	20	20	200
Cobalt	20	20	200
Copper	20	20	200
Iron	200	200	2,000
Lead	20	20	200
Manganese	20	20	200
Molybdenum	20	20	200
Nickel	20	20	200
Selenium	20	20	200
Silver	20	20	200
Strontium	20	20	200
Thallium	20	20	200
Thorium	20	20	200
Tin	20	20	200
Tungsten	20	20	200
Uranium	20	20	200
Vanadium	20	20	200
Zinc	20	20	200

NOTE: Final soil spike concentration based on the addition of 1.0 mL stock standard to 1.0 g of sample, which is then digested to produce a 100 mL final volume.

Attachment 1

Contamination Control Guidelines

The following procedures are strongly recommended to prevent contamination:

- All work areas used to prepare standards and spikes should be cleaned before and after each use.
- All glassware should be washed with 5% HNO_3 according to the procedure described in SOP DV-IP-0005.
- Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.
- Powdered should not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes.
- Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

The following are helpful hints in the identification of the source of contaminants:

- Yellow pipette tips and volumetric caps can sometimes contain cadmium.
- Some sample cups have been found to contain lead or cobalt.
- New glassware can be a source of silica and boron.
- Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.
- Improper cleaning of glassware can cause contamination.
- Latex gloves contain over 500 ppb of zinc.

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